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RESEARCH ON DEVELOPMENT OF LOW-RESISTANCE P-N JUNCTIONS IN ZNSE--ETC(U)

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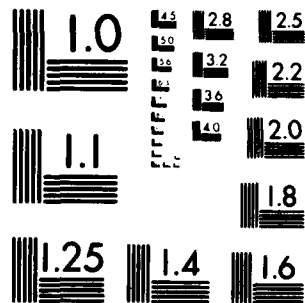


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FINAL REPORT
FOR
RESEARCH ON DEVELOPMENT OF
LOW-RESISTANCE p-n JUNCTIONS IN ZnSe

B. Fitzpatrick

Prepared for
NAVAL RESEARCH LABORATORY
Washington, D.C. 20375

Contract No. N00173-80-C-0175

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Prepared by
PHILIPS LABORATORIES
A Division of North American Philips Corporation
Briarcliff Manor, New York 10510

October 1981

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ABSTRACT

The doping problems associated with making a low-resistance p-n junction in ZnSe were investigated using modern epitaxial and implantation techniques. Substantial evidence for the role of nitrogen as a 'new' shallow acceptor with an ionization energy of 85 ± 5 meV was found, and a number of other acceptors were characterized. The behavior of background donors was studied; silicon and aluminum were found to be especially harmful contaminants. A ZnSe layer with a p-type conductivity of 1.5×10^4 ohm-cm was made. This is the lowest p-type resistivity in ZnSe for the case where the p-type character was definitely established.

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1. INTRODUCTION

The direction of this program was research leading to the fabrication of low-resistance p-n junction diodes in the II-VI compound semiconductor ZnSe.

The principal tasks were:

- (1) Identification of shallow acceptors.
- (2) Maximization of acceptor concentration
(target: 10^{17} acceptors/cc).
- (3) Identification and suppression of compensating donors
(target: $< 5 \times 10^{16}$ donors/cc).
- (4) Fabrication of low-resistance p-n junctions
(target: 10 ohms).

In general, Tasks (1) and (3) were essentially completed, but Task (2) requires more effort in order to achieve the goal of Task (4) viz., a truly low-resistance p-n junction diode.

In the past, it had been thought that ZnSe and other high-band-gap II-VI semiconductors could not be prepared with bipolar conductivity. Attempts to make ZnSe p-type resulted in compensated material, which was attributed to the formation of compensating centers by simple vacancies and interstitials. These simple defects have recently been shown to be unstable (Ref. 1). In addition, lack of suitable shallow acceptors also prevented good p-type conductivity. However, we believe that recent results by Philips Laboratories and others have changed the outlook for the control of conductivity in ZnSe.

Our approach was based on the application of the modern epitaxial techniques developed over the last decade for III-V compounds such as GaAs and GaP. However, in order to overcome the acceptor incorporation problem, more extreme conditions than those used for III-V epitaxy were used. These include the use of: liquid phase epitaxy at the highest temperatures ever, plasma activation of dopant species, and ion implantation to enhance the acceptor concentration.

2. IDENTIFICATION OF SHALLOW ACCEPTORS

The findings discussed in this section can be summarized as follows: nitrogen appears to be a good acceptor, phosphorus may have some potential, and arsenic and antimony do not seem to be of much use. Among the alkali metals, only sodium shows promise if its rapid diffusion can be minimized. The noble metals are deep acceptors.

2.1 Group V Acceptors

Previous work has indicated that nitrogen would likely be the best acceptor species. Unfortunately, nitrogen is very difficult to incorporate, and no reports of its incorporation other than by ion implantation have appeared in the literature.

To characterize the possible acceptor state formed by nitrogen, both optical (photoluminescence) and electrical measurements were used. In photoluminescence, a new bound exciton (BE) has been observed at 10.8 meV. (Bound excitons are electron-hole pairs whose binding energy is related to the depth of the center to which they are bound. They are observed as sharp lines close to the band edge.) This BE has been seen in material grown by liquid phase epitaxy (LPE) from both bismuth and tin solutions, by ion implantation and by vapor phase epitaxy (VPE) using plasma-excitation of nitrogen.

The observation of a BE correlated with doping by an element does not, however, provide conclusive evidence of a new acceptor state; corroborating data must be found. The donor-acceptor pair region of the spectrum provides additional data which support the hypothesis that a shallow acceptor state has been formed. (Donor-acceptor pair (DAP) transitions are due to electrons bound to donors recombining with holes bound to acceptors; thus, since the binding energy of donors is known, the energy of a donor-acceptor pair band can be used to determine the ionization energy of an acceptor state.) In both LPE and VPE, over a wide range of temperatures (275°C to 1125°C), a DAP band peaking at about 2.72 eV has been observed. From this, an approximate value for the ionization energy can be derived, viz., 85 ± 5 meV.

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The observation of p-type conductivity in as-grown or implanted material also buttresses the characterization of nitrogen as a shallow acceptor. p-type conductivity of about 10^5 ohm-cm has been observed in implanted material and in material grown from the vapor phase using plasma excitation to make the nitrogen more reactive and to enhance its concentration.

Also, secondary ion mass spectroscopy has shown the presence of nitrogen and has shown the diffusion of implanted nitrogen upon annealing for one-half hour at 600°C to be minimal.

Phosphorus was studied to determine if the shallow state seen earlier in LPE materials was reproducible. Despite the use of several different solvents (Bi, Sb, Sn, Te), various Zn/Se ratios (up to 10:1), and various cooling rates (0.5 to 21°C/min), the DAP band previously associated with phosphorus was not observed. No vapor epitaxy or high temperature (> 1100°C) LPE runs were done in this case; however, these techniques may have some promise for incorporating phosphorus in shallow-acceptor form.

No positive results were obtained with arsenic or antimony as dopants, although antimony may have some use as a solvent.

However, no evidence for the role of Group V dopants as deep acceptors has been seen. Thus, it is possible that ion implantation or other more drastic techniques may yet give good results.

2.2 Group I Acceptors

The light alkali acceptors, lithium and sodium, are known to form shallow acceptor states in ZnSe from earlier studies (Ref. 2). However, we realized that lithium would not be a good acceptor element since its diffusion rate at room temperature is too high. Sodium has a high diffusion rate at high temperature, but is relatively stable at room temperature. This indicated that the preferred method of incorporation would be ion implantation, although some growth experiments were done using sodium as a co-doping element along with nitrogen.

No acceptor state due to potassium or cesium has been obtained.

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Among the Group I-B acceptors, copper has the same difficulty as lithium, i.e., its diffusion rate is too high for practical use. In addition, its ionization energy is too high to be useful. Since silver has a lower ionization energy than that of copper in ZnTe (see Ref. 3), silver was incorporated in LPE. The same photoluminescence spectrum resulted in material grown from both bismuth and tin.

Unfortunately, the ionization energy of the silver acceptor was found to be 435 meV, and thus silver does not appear to be useful as a normal acceptor. This finding is supported by the electrical results which showed low p-type conductivity. Similar results were obtained for gold.

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3. MAXIMIZATION OF ACCEPTOR CONCENTRATION

In liquid phase epitaxy, high-temperature growth was shown to have some promise, but was very difficult experimentally. Vapor phase epitaxy at high temperatures had similar difficulties, but the use of plasma techniques at low temperatures produced interesting results, both electrically and experimentally. Ion implantation showed high levels of acceptor doping and the first measurement of the lateral conductivity in a confirmed p-type layer. However, the annealing-out of damage is as yet not understood.

3.1 Liquid Phase Epitaxy

Since, as explained in the preceding section, we believed that nitrogen was the most promising acceptor, effort was concentrated on finding new techniques to increase its concentration. In LPE, it was observed that the DAP band correlated with nitrogen appeared more readily in material grown from the vertical reactor when NH_3 was used as the doping source. NH_3 apparently does not have efficient contact with the melt in the horizontal case. To have more efficient nitrogen doping, solid Zn_3N_2 was put directly into the melt.

High-temperature LPE was tried in order to increase the solubility of nitrogen. Numerous experimental problems were encountered. Etch-back of the substrates was particularly severe, but was largely solved by changes in the melt composition and pre-heat cycle and by the use of cooling rates up to $20^\circ\text{C}/\text{min}$.

The results of these efforts (the highest-temperature LPE ever done, we believe) was the enhanced incorporation of nitrogen, as evidenced by the greater intensity of the 2.72 eV pair band. Only limited p-type conductivity (10^7 ohm-cm) was achieved. This may be due to the melt-back problem in which some impurities from the substrate are dissolved into the melt, while the substrate is being etched by an undersaturated melt, and are incorporated in the epitaxial layer when growth begins during the cooling cycle. This problem can be severe since our measured value of the segregation coefficient of aluminum is about 12, i.e., if enough aluminum is incorporated in the melt to give a concentration of 1 ppm, 12 ppm will

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be incorporated in the layer. The multiple-chamber feature of the LPE apparatus was used to address this problem, by starting the growth in one chamber and finishing it in another. However, auto-doping due to outdiffusion from the substrate into the growing layer at these temperatures and increased background contamination from the growth system have been difficult to overcome.

Several other solvents were tried in order to determine if incorporation of acceptors had improved. Antimony was tried since it is just above bismuth in the Periodic Table. We believe that this is the highest melting-point solvent ever used in liquid phase epitaxy. Nonetheless, the mechanical problem (solvent removal) was not a hindrance to growth. However, in the limited number of experiments that were tried, no obvious enhancement of acceptor concentration was seen, by either photoluminescence or electrical measurements.

In the case of zinc, no improvement in acceptor concentration was seen, either. However, since the material comes out strongly n-type, growth from zinc has potential to make material for implantation.

Tellurium was also used as a solvent since ZnTe is easily made p-type by incorporation of a number of well-established shallow acceptors. Formation of the alloy $\text{ZnSe}_x\text{Te}_{1-x}$ was suppressed by adding an excess of selenium to the melt. No obvious increase in acceptor incorporation was seen within the limited range of experimentation.

Magnesium was investigated as an isoelectronic dopant since it was felt that the ratio of incorporation of donors and acceptors might change under the influence of a reactive metal. No significant alloying was seen, i.e., formation of the compound $\text{Mg}_x\text{Zn}_{1-x}\text{Se}$, as judged from the position of the sharp BE lines observed in photoluminescence. No significant effect on the relative incorporation of acceptors and donors was seen, either.

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3.2 Vapor Phase Epitaxy, Including Plasma Doping

We had noticed that material which deposited on the walls of the LPE tube was luminescent. Polycrystalline material was also occasionally deposited on the end of the graphite slider, and this showed the nitrogen DAP spectrum upon photoluminescence examination. Therefore, we decided to place a substrate wafer at the end of the slider to see if vapor epitaxial growth would result. This was apparently the case, since the characteristic oriented triangular hillocks of VPE were seen. The nitrogen DAP spectrum was seen in this material when either N_2 or NH_3 atmospheres were used. This is surprising since nitrogen is generally regarded as unreactive: in fact, no evidence for nitrogen incorporation out of nitrogen gas at atmospheric pressure was seen with substrate temperatures less than $1000^\circ C$.

To enhance the reactivity of nitrogen in the vapor phase, plasma excitation by means of a capacitively coupled audio-frequency discharge was tried. Because of the strong etching effect of the plasma, growth was only successful at temperatures lower than $725^\circ C$. Runs were performed at temperatures as low as $175^\circ C$; the best results appeared to be in the 325 to $475^\circ C$ range. In this method, for the first time applied to any II-VI semiconductor in our knowledge, the BE, the DAP band and p-type conductivity of $\sim 10^5$ ohm-cm were seen. Work on this technique was only begun in the last four months of the contract; these initial experiments showed the power of this technique, despite the relative crudity of the apparatus.

3.3 Ion Implantation

Although ion implantation had been tried before (Ref. 4) in order to type-convert II-VI compounds, we felt that improvements could be made in its application by using epitaxial material and by using the improved annealing techniques developed over the last several years.

Implants were done in three facilities: Philips Laboratories, the Naval Research Laboratory (H. Dietrich), and the University of California, Santa Barbara (J. Merz). The energies used were in the 40 to 300 keV range, and fluences ranged from 3×10^{12} to 10^{17} atoms/cm².

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Most of the effort was concentrated on nitrogen, although a few phosphorus runs were made. None of phosphorus-implanted samples showed conclusive evidence of p-type conductivity; only relatively low fluences were used, however (3×10^{12} and 3×10^{14} atoms/cm²).

Since nitrogen is a very light atom, its range in ZnSe can lead to a relatively deep junction (0.8 μ m at 200 keV, according to the LSS [Ref. 5] calculation). SIMS (secondary-ion-mass spectroscopy) profiles confirmed this number, both before and after annealing at 600°C for 30 min. This indicated that at this temperature, at least, appreciable outdiffusion did not occur.

Initial annealing studies concentrated on material implanted with moderate fluences (1 to 3×10^{15} /cm²) of nitrogen. These experiments indicated that the optimum annealing schedule was 700°C for 15 min in flowing nitrogen. Upon re-examination, these studies have shown that the optimum annealing conditions have not yet been achieved; however, a starting point for further work is the 700°C/15 min./flowing N₂ schedule.

The dose dependence of the electrical conductivity was investigated in the 10^{12} to 10^{15} ions/cm range. Higher doses were used, mainly to determine the amorphization threshold, and have not yet been evaluated. At present, there is no clear indication of the optimum dose. The best resistivity obtained was 1.5×10^4 ohm-cm.

In this case, as well as in the plasma case, the activation energy of the conductivity showed that the presence of a deep acceptor at 0.7 eV was controlling the conductivity by Fermi level pinning. Thus, it appears that an appreciable number of shallow acceptors must be present. Calculations indicate that the total number of acceptors (N_A) is greater than 10^{18} /cc.

This is the first case, we believe, of the measurement of the lateral conductivity of an implanted layer in a II-VI compound where the measurement provides direct confirmation of the p-type character of the implanted layer.

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4. IDENTIFICATION AND SUPPRESSION OF COMPENSATING DONORS

The most important contaminants were studied in order to find sources of compensation. Aluminum and silicon were found to be particularly harmful. The light elements, anionic species, and transition elements were found to be relatively unimportant.

4.1 Aluminum

A number of potential background contaminants which could be strong sources of compensation were studied and also investigated for use as donors. Aluminum was found to be a particularly harmful contaminant, because of its high segregation coefficient and apparently high outdiffusion rate from the substrate under most growth conditions (see Sect. 5). The addition of even the smallest amount of aluminum (0.2 mg in a 8 g melt) resulted in a smearing and reduction in intensity of the near band edge spectra and the appearance of a very large amount of deep level emission. This emission is caused by the presence of the $V_{Zn}-Al_{Zn}$ complex which is a deep acceptor. The formation of this complex reduces the efficiency of aluminum as a donor; larger additions (5 mg) are needed to give conductive material ($n = 8 \times 10^{15}$ electrons/cc).

4.2 Silicon

In the past, silicon was thought to be electrically inactive in II-VI compounds. However, since it is a difficult-to-avoid contaminant in growth systems, we felt it should be investigated. Silicon was found to be a strong donor: additions of 0.2 mg to a 50 g bismuth melt resulted in donor concentrations of 3×10^{16} /cc. Similar results were seen in material grown from tin solution. No specific deep state could be definitely associated with silicon. Normally, silicon could be a double donor when substituted for zinc, and a double acceptor when substituted for selenium. However, the empirical evidence suggests that the net effect is to increase the concentration of single donors. A possible mechanism for this is the formation of $Si_{Zn} - (Li, N_a \text{ or } Cu)_{Zn}$ complexes which would be single donors.

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It is surprising that silicon has been ignored as a strong cause of compensation. A chapter by Woodbury in "Physics and Chemistry of II-VI Compounds", Aven and Prener, eds., (Ref. 6) states ... "Silicon is always seen in mass spectrometry analysis in varying concentrations and would appear in most cases to be electrically inactive." E.p.r. studies (Refs. 7,8) have only shown silicon on the zinc site where donor action is expected. Silicon is a common contaminant in most growth systems, and quartz ampoules (Ref. 9) and tubes (Ref. 10) have been used by most investigators. These LPE samples are grown under near-equilibrium conditions from two different solvents, so it is unlikely that this phenomena is unique to our experience. As a result of this study, particular attention was devoted to the reduction of the sources of silicon contamination. Graphite and boron nitride crucibles were used for growth, and, where possible, cold-wall reactors (radiant furnaces) were used. (Potential problems of contamination from carbon and boron nitride are addressed below.) In addition, normal glassware was replaced by vitreous carbonware for substrate preparation. Analysis of boats and LPE melts showed concentrations in the 4-30 ppm range. To alleviate this problem, boats were changed more rapidly than before. Using laser-source mass spectrometry, values of less than 0.25 ppm atomic were seen.

4.3 Carbon

Carbon contamination was investigated by growing LPE layers in a boron nitride system with and without added carbon. No difference in the spectra could be discerned upon addition of carbon. Electrical measurements showed that the conductivity type of the carbon-doped material was indeterminate. Secondary-ion mass-spectroscopy (SIMS) showed a low carbon signal (100 counts per second); although this signal was uncalibrated, it is likely that the carbon concentration was low. This is not too surprising since the solubility of carbon in ionic materials is generally low.

4.4 Boron

Boron appears to be a good shallow donor since the good spectral properties of undoped material are preserved even at relatively high additions of

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boron (2 mg B in 50 g Bi). This may be due to the apparent lack of formation of $(V_{Zn}-B_{Zn})$ centers which, being acceptors, would drastically reduce the net donor concentration. Chlorine is an intermediate case: the conductivity indicates relatively low doping efficiency, and the strong emission from $(V_{Zn}-Cl_{Se})$ centers is seen, but the near band edge spectra are reasonably well preserved. Neither of these species appears in very significant quantities in mass spectra, generally being much less than 0.1/ppm. However, some vigilance was needed to keep them at low levels, e.g., no HCl was used in cleaning procedures, and borosilicate glass was replaced by vitreous carbonware in wafer processing.

4.5 Growth Atmosphere

Argon and hydrogen were compared as growth atmospheres. No difference was detected in the spectra, and thus, except in cases where nitrogen or ammonia were used for doping purposes, argon or helium was substituted for hydrogen as the growth atmosphere. The oxygen content of the argon was found to be less than 0.5 ppm, so that no deleterious effects on the layer growth had been observed. Although there does not seem to be a primary effect of hydrogen, there can be a secondary doping effect due to the reaction with the quartz walls: $SiO_2 + H_2 \rightarrow SiO + H_2O$. This reaction eventually leads to silicon doping.

4.6 Hydrogen and Hydroxyl

Hydroxyl doping was tried, since the hydroxyl ion (OH) is a well-known donor in zinc oxide. Cesium hydroxide was used as a source, since zinc hydroxide is unstable at any reasonable growth temperature. No strong deleterious effects appeared in the spectra, and, upon implantation, the material became p-type.

In SIMS analysis, since only relatively low count rates (200 cps) were seen, it does not seem that hydrogen, either bound to selenium or to oxygen, is an important cause of compensation.

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4.7 Transition Elements

Segregation coefficients for a number of common impurities were determined (Table 1). The grown material was analyzed by laser-source mass spectroscopy, and the corresponding melts were analyzed by emission spectroscopy. These coefficients are subject to large errors. Also, the study was only done with tin as a solvent. However, the results show that aluminum is a particularly difficult element to control. The high segregation coefficient for manganese should not be of too much concern, since manganese is generally considered to be isoelectronic.

TABLE 1

| <u>Element</u> | <u>Segregation Coefficient</u> |
|----------------|--------------------------------|
| Al | 12 |
| In | 0.2 |
| Fe | ND* |
| Si | 0.1 |
| Mn | 400 |
| Cr | 0.2 |
| Ga | 0.006 |
| N | ND* |
| Cu | 0.003 |

*ND: not detected

5. FABRICATION OF LOW RESISTANCE p-n JUNCTIONS

Diode characteristics were measured on material fabricated on an n-type substrate. The results were disappointing, but we believe the most important problems have been identified.

Most of the work of this program was devoted to the growth and implantation of p-type layers, without concern for the electrical characteristics of the underlying material. In fact, it is much easier to prepare p-type material on an undoped substrate than on an aluminum-doped n-type substrate. This is probably due to autodoping from the substrate, which can take place in two ways: (1) etch-back of the substrate and subsequent incorporation of n-type dopants into the growing layer, and (2) outdiffusion of n-type dopants into the layer as it grows. The first case may be prominent in LPE; multiple chamber boats were used to do the etch- or melt-back in one chamber, and the growth in the next chamber. Sometimes, a buffer layer was grown to isolate the p-type layer from the substrate; in this case, not only did the etch-back take place in a prior chamber, but the effect of the outdiffusion was reduced because the p-type layer was separated from the substrate by the buffer layer. This method appears to give material with the best spectra, but, to date, we have not confirmed its effect on the electrical properties.

In VPE, where the outdiffusion effect would be expected to be more prominent, growth at low temperatures should make it possible to grow p-type material on aluminum-doped substrates. However, most attempts resulted in n-type material, or p-type material of greater than 10^6 ohm-cm resistivity. Recently, however, in order to circumvent this difficulty, we used substrates which were nominally undoped, but annealed in zinc to make them n-type conductive. This allowed us to make p-type material on an n-type substrate, which is, of course, necessary for making a grown (i.e., non-implanted) p-n junction diode. Using this technique, we made diodes with a forward voltage of 13 V at 10 μ A and a reverse voltage of 50 V at 10 μ A. The high resistivity may be the result of degradation of the substrate by the plasma before the deposition really gets started during the run.

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6. SUMMARY

Of the potential acceptors investigated, nitrogen was the most promising because of its suitably shallow level (85 meV) and low diffusion rate. Among the other Group V elements, only phosphorus showed any promise. Among the Group I elements, sodium may be useful since its diffusion rate at room temperature is very low. Lithium has a high diffusion rate at room temperature. No manifestation of acceptor behavior has been seen in the case of either potassium or cesium. Copper, silver and gold are deep acceptors.

The concentration of nitrogen acceptors in ion implanted material was estimated to be at least 10^{18} /cc. In as-grown material, this number is probably considerably lower. The lowest resistivity achieved so far has been 1.5×10^4 ohm-cm in an implanted sample. The resistivity of as-grown material is roughly comparable. In addition, diode rectification was seen.

Of the background contaminants studied, silicon and aluminum were found to be important sources of compensation; the other elements examined did not seem to be significant.

Pertaining to further work, the most immediate results could be obtained by optimizing the implant parameters, especially annealing. This includes laser, electron-beam, and microwave annealing. The use of epitaxial wafers grown especially for implantation would assist this work. Some effort on other ions such as phosphorus may be worthwhile.

Improvement of the plasma VPE would be promising, since only a fairly crude method of excitation (a Tesla coil) had been used. Also, since this type of vapor epitaxy is different from ordinary vapor epitaxy in its pressure and temperature conditions, more effort is needed to master its application to ZnSe. Specifically, the growth of thick layers needs to be achieved, so that the properties can be studied in more detail. Other dopants such as phosphorus and sodium should be tried by this method.

In liquid phase epitaxy, the very high temperature and rapid cooling capabilities of the radiant furnace could be more fully exploited.

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